CALCIUM SCALES – SCRAP SCALING INDEXES AND THE CONCEPT OF SUPERSATURATION

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ABSTRACT

Data are presented that show that scaling by calcium/magnesium salts from recirculated evaporatively cooled waters is a production process, commonly of low efficiency, which is governed by engineering- as well as chemical- parameters. It may be considered as a two part process – precipitation (loss from solution) and deposition (nett adhesion of part of the precipitated material). It can be quantified by subtracting the scalant effluent mass from the scalant influent mass. Circulating water is shown to not exhibit bulk super-saturation nor to have an industrially important induction period for the production of scale.

Peter Drucker [1], a Management Theorist, promoted the concept that, "You cannot manage what you cannot measure". This paper sets out how to measure scale precipitation and deposition for two scales: calcium phosphate and calcium carbonate.

INTRODUCTION

Calcium carbonate scaling is not a new phenomenon. It was a problem that led to Roman aqueducts suffering reductions in water flow to its cities and to subsequent high maintenance costs [2].

By the 1920s, calcium carbonate Scaling Indexes [3], [4], [5], [6], were being derived from chemical analyses of domestic water supplies. Initially, their use was to identify corrosion conditions that led to brown domestic water supply; it was observed that calcium carbonate scale inhibited corrosion of cast iron pipes. Scaling Indexes are at best a qualitative indicator of a water's propensity for scale precipitation. It was not possible then to differentiate between such water entering a *pipe* and that leaving, and it still is not. But it is possible to quantitatively differentiate between water entering and leaving an industrial *system*. This concept facilitates the calculation of the mass of scalant being precipitated within that system, Hawthorn [7], [8], [9] and [10], with Wilson.

As with any production process, the mass of product depends on the mass of raw materials entering (in this case calcium salts) and the transformation by the process, in this case elevation of its temperature, its pH (in the cooling towers) and the removal of some of its solvent (by evaporation).

To account for different design procedures and operational problems, heat exchangers may have an allowance of 30 to 50% for fouling [11]. This paper will promote the concept that the parameters which control scaling can be reliably quantified, thus reducing over-design and aiding with operational control.

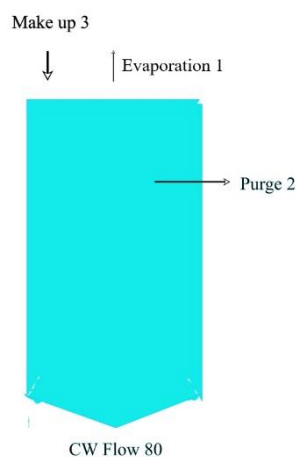## THE DESIGN OF A POWER STATION COOLING WATER SYSTEM

Figure 1. This illustrates that the Purge is an aliquot of the Circulating Water. The arrows width is proportional to flow rate. It can be seen that an analysis of Purge Water is identical with that of the Circulating Water and vice versa.

Typically, for a concentration factor of 1.5, the ratios of flow rates were: evaporation, 1; purge, 2; make-up (input) 3; circulation, 80 (see Fig. 1). The Figure shows why sampling the circulating water (CW) alone cannot indicate a scaling rate. The CW has the same analysis as the Purge. Thus, Scaling Indexes, no matter how refined, cannot quantify a scaling rate.

Engineering parameters may affect time for precipitation and/or deposition.

The half-life of water in the system, which is the time required for its mass to reduce to half of its initial value, is calculated from

$$t_{1/2} = -\log(1/2) \text{ SysVolume } / \text{ Make Up Rate} \qquad (1)$$

i.e. it depends on the volume of the system.

The number of times N an increment of water will pass through the heated tubes before discharge

N = -log (1/2) C / V x (V / M) so
N = -log (1/2) CW flow rate / Make Up Rate   (2)

It is the ratio of cooling water flow rate divided by the make-up rate and is independent of pond size.

CALCIUM PHOSPHATE – THE PROBLEM

In the 1950s until its privatisation in 1991, the UK's Central Electricity Generating Board (CEGB) emphasis was on large generating units with large natural draft cooling towers, chosen for their efficiency (no fans consuming power). Experience had shown that, provided the concentration factor (CF) of the recirculating cooling water did not exceed 1.5, calcium carbonate deposition on the condenser tubes did not produce an operational problem. It was a surprise therefore in the 1970s when the condensers of new power stations along the river Trent, despite operating at CFs of 1.5, began to experience impairment of heat transfer due to a new scalant, calcium phosphate.

It was expected that the Taprogge Process, [12], could provide an engineering solution to calcium phosphate scaling but that it could not be installed in all affected power stations for some years. In the meantime, the Chemistry Section of the Scientific Services Department of the CEGB's Midlands Region was tasked with testing commercial scale ameliorants, even though they had been produced for calcium carbonate scales.

CALCIUM PHOSPHATE - RIG STUDIES

Despite criticism and doubts that scale could be grown in a rig, a twin circuit rig was constructed which modelled two condenser tubes (Admiralty brass ex Cottam P.S.) in a low-pressure steam-heated environment and two temperature controlled forced draft cooling towers, to test heated concentrated river water against the same with the added ameliorant under test. See Figure 2.
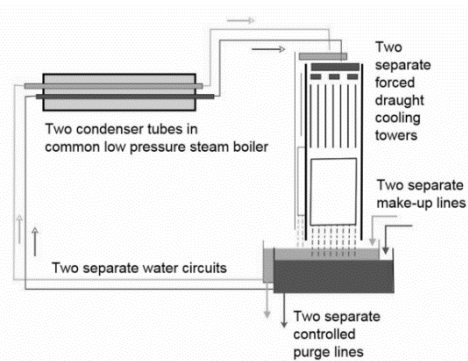

Figure 2.   Schematic of the CEGB scaling rig

Each experiment was in two parts. Part 1 was continued until the CW had risen to the concentration required for the run. The heated tube was then removed, and acid cleaned. Part 2 was run under constant CW conditions maintained by purging the CW and constantly adding river water to replace the water lost in the purge and by evaporation.

Other chemists were trying to create an Index for pH of saturation of phosphates based on one published by Green and Holmes, [13] in 1947, namely the KRW Index. Like other Indexes it was based on an analysis of the circulating water, which has been shown to the same as the purge water, and hence created a poor fit. See Figure 3.
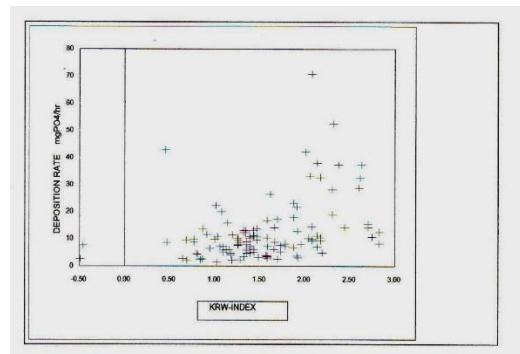

Figure 3 KRW Index vs Rig Derived Deposition Rate. $R^2 = 0.14$

The scaling rate of un-dosed river Trent water was used later to create algorithms for precipitation of calcium phosphate (loss from solution) and deposition (adhesion of part of the precipitated material onto heated surfaces). The first demonstration of the rig's response to influent mass is shown in Figure 3, when river water from different seasons (containing different levels of river-derived influent phosphate) needed a different input mass to achieve similar circulating water (CW) concentrations, as in Table 1. These similar CW conditions did not produce similar deposition rate

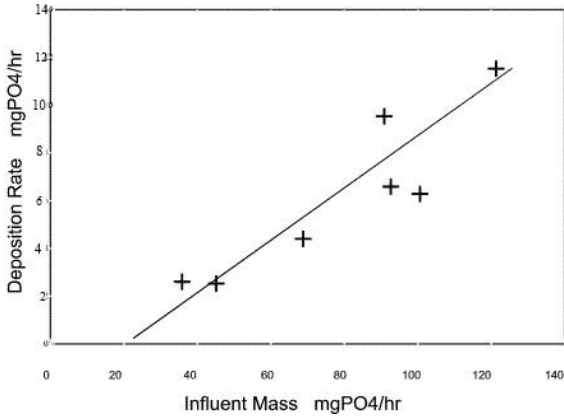but showed a correlation with the influent mass of phosphate.

Figure 4. Rig observations: deposition vs influent mass of phosphate for similar experimental conditions. Operating conditions summarised in Table 1.
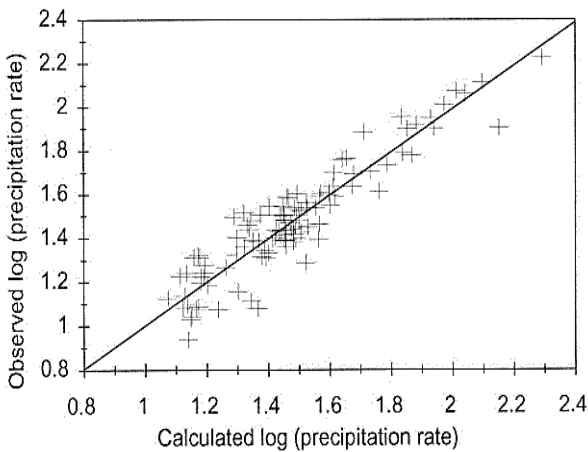

Figure 5. Agreement between measured precipitation mass rate and fitted result (Equation (1)). Solid locus shows a line of equality.

Table 1. Operating parameters for tests in Fig 4.

Parameter	Value
T_{in}	23.1 ± 0.2 °C
T_{out}	32.3 ± 0.3 °C
pH	8.38 ± 0.03
[PO$_4$] in cooling water	6.6 ± 0.3 mg/l
[Ca] in cooling water	158 ± 6 mg/l
Mass flow rate of PO$_4$ in feed	36-122 mg/hr
Flow Rate through 1" tube	6 litres/minute
Residence time	11 seconds

PRECIPITATION

Using the results from over 100 experiments, an algorithm was developed that linked the mass precipitated (M) with the mass of influent phosphate, pH, T, calcium in the CW and half-life of scalants in the system: -

$$LogM = 1.22\log (Q \times [[PO_4]_{IN}-2/CF]) + 0.23pH$$
$$+1.10 \log [Ca]_{CW} + 1887\{1/273 - 1/(273 + T_{OUT})\}$$
$$+ 0.165 \log t_{½} - 5.896 \qquad (3)$$

The factor -2/*CF* allows for dissolution of pre-deposited scale when the concentration of scalant in solution in circulating water is less than saturation, at around 2 ppm, which could arise in winter. This relationship contains expected trends, such as increasing precipitation with the influent phosphate mass, pH, temperature, and calcium concentration. It had a Correlation Coefficient $R^2 = 0.87$ for the hundred plus experiments. See Figure5

The coefficient of 1.1 for calcium is a surrogate for the additional magnesium also precipitating as the phosphate.

DEPOSITION

Applying a similar approach to the deposition rate, D, gave Figure 6 where

$$LogD = logM + 0.5pH + 0.025 (T_{OUT} - T_{IN})$$
$$+0.15 \log t_{½} + 1.5logRe - \log \tau - \beta \qquad (4)$$

where β is a factor which varies between the 20,000 tubes in the condensers on the plant (presumed to be due to differences in heat gain).
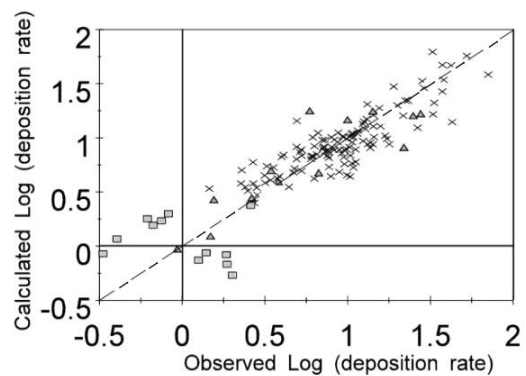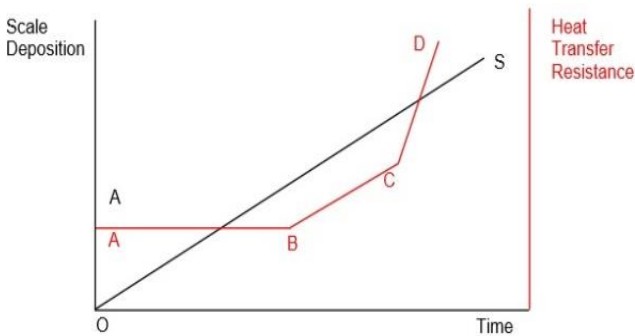

Figure 6. Regression of estimated deposition rate (Equation (2|)) and that based on measured adherent

scale. $R^2 = 0.80$. Dashed solid locus shows a line of equality. Symbols indicate tube i.d: crosses - 23.1 mm; triangle – 15.9 mm; square – 7.9 mm.

River Water Simulation

It had been postulated that the reason that observed scaling from river water did not correlate with the KRW index was that river scaling was being enhanced by a mixture of low levels of manganese (<1ppm) and also reduced by fulvic acids. This was disproved by comparing river water in one circuit with water of similar analysis prepared from deminerailised water, Analar chemicals and carbon dioxide (to dissolve calcium carbonate the way rain does). The scaling rate was the same. This means that a river water can be simulated and scaling can be studied anywhere, not just on a river bank, and that it is the Index approach that is wrong, not the water composition.
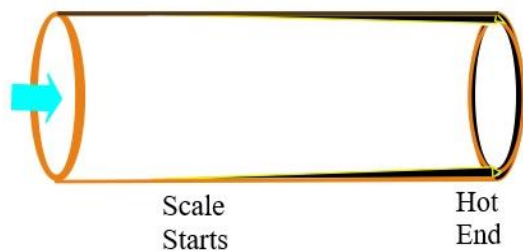
The topography of scale

Figure 7. This is an illustration of scale deposition tapering along the length of the tube.

Early-stage scale deposition shows more scale deposited at hot end of tube and none at the cold end in Figure 7. It shows that scale deposition cannot be described in terms of mass per unit area, only mass per tube. It was constructed from observation of a Cottam PS actual condenser tube.

Thermal Effects of Scale Deposition

Figure 8. Plot of scale deposition (OS) and Heat Transfer Resistance (AD) against time, [14]

Figure 8 shows that when scale deposition is constant (OS), it will not produce constant heat resistance. It shows that a there is no change in heat transfer resistance (AB) whilst there is some internal surface that is not covered in scale; that there is a constant increase in resistance (BC) whilst the scale is thin enough to transfer all the heat supplied to it but that when the scale thickness passes a critical point (C), the impairment of heat transfer increases at a high rate (CD).

Different allowances for scaling from interpretation of TEMA codes, different shear stress or different surface structures would affect the length of time of AB. Different surface treatments could affect the slopes of BC and CD.

It illustrates why previous papers Epstein, [15] Bott, [16], that have relied on heat transfer impairment as a measurement of scale deposition may need to be re-examined. Previous reports of induction periods may be due to thermal detection methods being used which are influenced by generous areas of heated surfaces. Chemical analysis methods are capable of detecting scale early before it has an effect on heat transfer. The power stations that reported scaling only did so after efficiency losses were noted. Chemical analysis of circulating waters was only used by station staff to generate a scaling index which was not quantitative and was not interpreted as detecting scale precipitation or deposition in the condensers.

In the Trentside 2000MW stations the "Induction period", when there was no observed heat transfer impairment, lasted for over a year and this knowledge was used by detractors to argue that the rig would not be capable of assessing scale inhibitors in a useful time.

Amongst the first experiments performed was a group of three, using River Trent water and lasting for 24, 48 and 68 hours respectively to see whether a reasonable period for test could be established. The deposition results can be seen in Figure 9. It was not meant to establish an induction period *per se,* but established that a reasonable period of three days at constant conditions would be reasonable to assess and compare different scale inhibitors. It does, however, show that a long period for scale induction
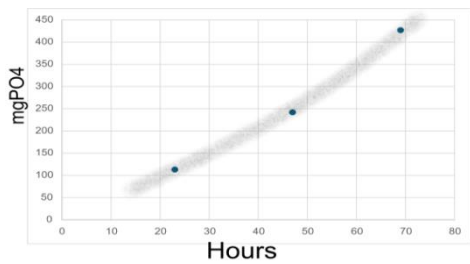
does not eexist.

Figure 9. An Insignificant Induction Period

CALCIUM CARBONATE
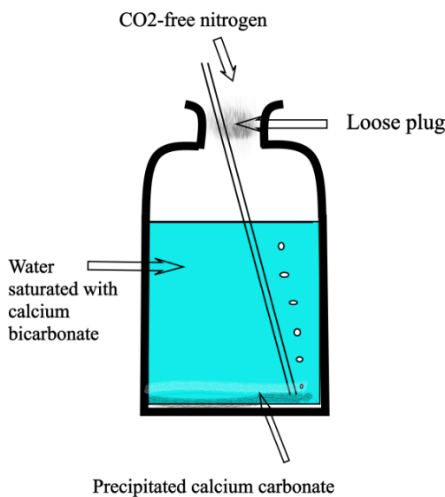
Laboratory Study of Super-saturation

Figure 10 Sparging apparatus.
Room temperature sparging by nitrogen to remove carbon dioxide during AB, CD and EF. Gas sparging was stopped over weekends at BC and DE.

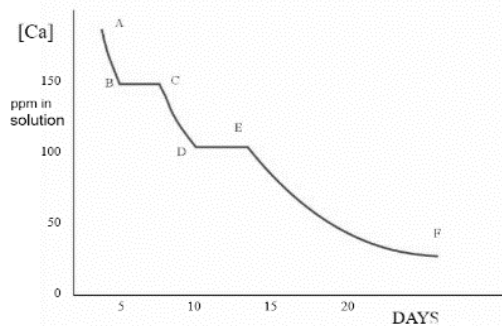$$Ca(HCO_3)_2 - CO_2 = CaCO_3\downarrow + H_2O \qquad (5)$$

Figure 11. Effect of CO2-free nitrogen sparging on an aqueous bicarbonate solution shows that calcium bicarbonate is stable in solution when sparging is stopped. The solution is not supersaturated.

Using the equipment of Figure 10, the results are shown in Figure 11. This simple experiment showed that calcium carbonate/ bicarbonate does not exhibit bulk super-saturation (there was precipitated material always beneath the solution) as the samples are stable, showing no sign of spontaneous precipitation, for at least weekends, if not longer. Bulk supersaturation of calcium carbonate is not a problem; it does not exist. But it also shows that the solubility of calcium bicarbonate is not a constant at a given temperature; it approaches equilibrium with the gas above it, but that approach is slow even with nitrogen; with air containing carbon dioxide the precipitation of calcium carbonate would be slower.

CALCIUM CARBONATE - A PRACTICAL PROBLEM

The Effect of Concentration Factor

French Nuclear power stations are mainly sited on rivers and in 2019, and since, the river authorities have restricted the discharge of heat to the Garonne, Rhone, and other rivers, [17] Restricting a station's heat discharge to a river can only be done by restricting its purge and this will increase its cooling water concentration as illustrated in Table 2, unless the station restricts production.

Table 2 was constructed to show how the purge rate from a 500MWe unit is governed by the system concentration factor. It shows how the effluent mass and influent mass of water (and scalants) decreases as the concentration factor increases.

Using   Purge = Make Up – Evaporation
and   Concentration Factor =Make Up / Purge,
1MWhr will evaporate 1,470 litres or 1.47 tonnes.
A 500MW$_{electrical}$ unit needs to reject 660 MW$_{thermal}$ and 660MWhr will evaporate 972 tonnes of water.

Table 2. Water Use of a 500MWe generating unit. Assumes 10 degree C rise in temperature from ponds.

CF	Make-Up tonnes/hr	Purge tonnes/hr	Heat (MW) Discharge to river Per hour
1.0*	54,500*	54,500*	660*
1,5	2,910	1,940	22.6
2.0	1,940	970	11.3
3.0	1,455	485	5.7
4.0	1,293	323	3.8
5.0	1,212	242	2.8

6.0	1,164	194	2.3
7.0	1,131	161	1.9
ZLD	971	0	0

*   This data represents a once-through system, i.e. one with no evaporative cooling; only used in coastal or large estuarine locations.

ZLD is zero liquid discharge, when all salts are retained in the system and all heat is released to the atmosphere by evaporation of influent water. It is shown, so that it can be seen that ZLD reduces the heat discharged to the river by a small amount, compared to say, a CF of 3.0 (and will cause significant scaling problems en route).

However, the scalant production efficiency increases with CF (or time, or number of times that they pass through the heated area), see Table 3.

Table 3. The Effect of Concentration Factor on Calcium remaining in solution and the mass of calcium precipitated per hour. Rig results from water with different influent calcium concentrations

CF	Ca-Inlet mgCa/l	Ca-CW in solution	% Ca precipitated/hr
1.13	69	78	0
2.14	82	160	10
3.79	91	229	52
6.10	72	335	76

Referring back to Table 2, it can be seen that an increase in CF, due to a decrease in purge, reduces the heat discharge to the river.
The increase of CF is accompanied by a reduction in the heat discharged from the receiving water course but beyond a CF of 3 the benefit diminishes rapidly, and the scaling problems increase equally rapidly.
Nevertheless, discharging 130MWs less when changing from a CF of 1.5 to 3 may well allow a 500MW unit to continue working compared to taking it offline.

RIG STUDIES

Calcium Phosphate Rig
The 1/10th size (of a single tube of a typical 500MW$_e$ power station condenser), i.e. 1.83m cf 18.3m)
The rig's main characteristics are
(1) that the water under investigation is heated by a vapour at a temperature lower than the boiling point of water, so that any scale that forms in the heated tubes is not pushed off by bubbles of steam being generated within the flowing water under test, which is at a little over atmospheric pressure,
(2) that the water under test is concentrated by evaporation in the cooling tower, not by the addition of chemicals such as sodium bicarbonate and calcium chloride which would have had different kinetics.
(3) that there is make up and metered purge to control the concentration factor,
(4) that the circulating water resides in the heated tube(s) for a period that is within industrial design (c.11 seconds).
(5) that there is no risk of legionella forming, so the circulating water is exposed to UV light and the cooling tower packing is "anti-legionnaire" to protect staff and neighbours.
(6)   Detection and analysis of scale was performed chemically at the end of an experiment (washing of tube with c.2% HCl and subsequent analysis for phosphate and calcium), and no induction period was observed.

Calcium Carbonate Rig

The author thought that the rig study of calcium carbonate would merely provide different values for similar parameters from those in the Precipitation and Deposition algorithms for calcium phosphate, but this was not true. The processes appear to be quite different.
The construction of the single circuit rig was delayed by Covid affecting supply of components.
The operation of the rig was affected by a tripling of the price of electricity due to the Russian war against Ukraine and the fact that this study received no financial support from industry or academia and was funded privately. Thus, the experiments are few and Proof of Concept only and cannot by themselves produce useful algorithms. They are sufficient to show that the influent mass of scalants is important, as in any production process, and to identify some of the parameters that control the efficiency of the scale production process.
Traditionally, operating PSs at a concentration factor of 1.5 has caused no operational problems due to calcium carbonate scale. But the solubility of calcium carbonate will depend on pH and temperature as well as the influent composition before concentration. So one would expect a system with low influent concentration of incipient scalants to be able to operate at a higher concentration factor than a system fed by influent water with a high level of scalants. Thus, concentration factor itself is not easily incorporated into the science of precipitation; solubility is.

The rig is shown in Figures 12 and 13.

Figure 12. The vacuum boiler

There are some difficulties when working from home that do not occur in a well-equipped laboratory. Purchase of analytical grade chemicals is one (particularly difficult in the UK) and, in this case, provision of drainage. Gravity drainage requires a head and a drain at floor level (neither were available). So, purge needed to be pumped (rather than using a gravity-fed lock-hopper device). The solution to the problem was a second-hand variable peristaltic pump. This proved to be an economy too far. It was unreliable and responsible for most of the curtailment of experiments.

These experiments were conducted using Severn Trent domestic water (sulphate less than 2mg/l), so calcium and magnesium are mainly associated with bicarbonates. See Table 3 for the variation in calcium in the influent water. Magnesium could not be determined in the absence of required EDTA indicator but, from river Trent analogy, is probably around 10% of the determined calcium concentration.
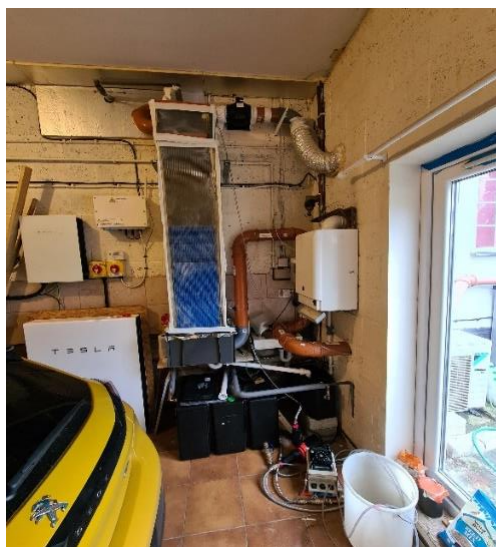

Figure 13. The Cooling Tower.
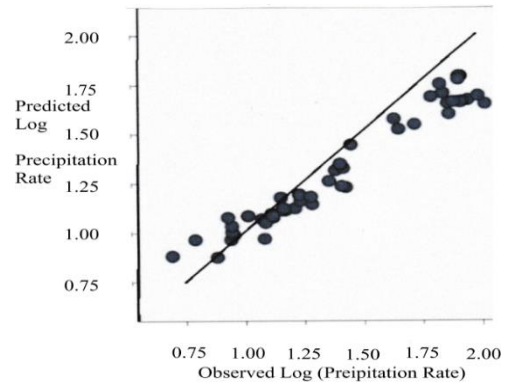
Rig Results

Precipitation

Figure 14. Log (Ca Precipitation rate) regressed against Log (Ca In), Log (Concentration factor), pH and T (Out).

Figure 14 shows that although there is a near linear relationship between the amount of calcium precipitated (lost from solution) and the influent mass of calcium, the concentration factor, pH and temperature of water leaving the heated tube, the line of equality does not fit the data very well. Including the half-life (see Equation 1) or the number of times that an aliquot of water passes through the heated tube (see Equation 2) did not improve the fit.

Solubility

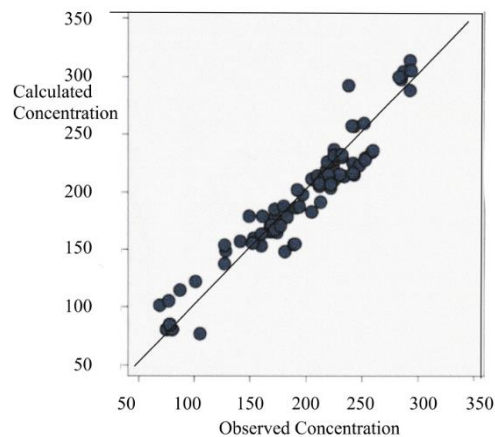
Figure 15. Concentration of Ca remaining in solution regressed against CF, T and pH.

This relationship raises the question, is scaling best defined by studying the solubility of that scale under simulated industrial conditions (temporal solubility time). But, earlier, Figure 11 shows that solubility depends on how much carbon dioxide has been removed from bicarbonates, hence the Figure

120

15 plot may be rig-specific with only one cooling tower configuration used in the experiments.

The Effect of pH and Alkalinity

It is possible that pH (so long an indicator of conditions that control precipitation) is an *effect* of the scaling process (calcium alkalinity offset by atmospheric carbon dioxide), and not the *cause* of precipitation.

In every experiment, calcium carbonate was observed to have been deposited in the pond and some on the cooling tower pack, thus deposition on heated tubes (which is the main concern as it impedes heat transfer) is always less than precipitation.

Normally, in industry, temperature and pH are confounded. As the temperature is raised, more carbon dioxide is displaced from bicarbonates and so the pH is raised.

Quantified knowledge is fundamental and this Concept of determining the mass of scalants can be developed in two ways. One, directly by quantifying all the parameters affecting precipitation, but, by analogy with Equation 1 for phosphate precipitation, not enough experiments have been performed yet. The other by studying solubility (what doesn't precipitate).

DISCUSSION

The outcome of this work will affect several areas of knowledge, reducing uncertainties and improving TEMA codes and also the reduction of over purging and reducing the power needed to supply excessive influent water, particularly in winter when the additional power generated can be sold at a premium.

No quantitative algorithms are presented here due to the paucity of data but when further experiments have been completed under more stable conditions, algorithms will enable designers to optimise condenser specification.

Not only that but, as most systems will have a history of analysing influent and circulating water (now seen as the same as the purge water) it is possible to quantify previous plant deposition data. Chemical engineers can examine the initial specification to quantify over design and so can confirm to plant operators how much of any excess can be safely used in future.

The concept presented here will enable plant chemists and engineers to quantify scaling by subtracting the effluent calcium (CW or purge) mass per unit time from the influent mass of calcium per unit time. Because of the unchanging nature of the parameters which govern deposition (hydraulic flow conditions and tube diameter are constant for any one system), it may be convenient to assume a

percentage of the mass precipitated is deposited on these heated surfaces.

It is acknowledged, [18] that scaling is a world-wide expensive problem manifested in reduced heat transfer and over-design at the commissioning stage.

Under-design would create long lasting costs, so an allowance is built into the TEMA codes to counter the unknown rate of scaling and silt deposition. It is time that scaling could be quantified in advance for any new site to reduce unknowns.

One reason for quantifying the parameters which control scaling is for operators. The inbuilt over design of existing stations is available for use. The onset of scaling should be monitored for its rate and radical steps for its amelioration should not be taken at the first sign of scaling, but the available excess of heat transfer area should be utilised first.

The other reason is that the concentration factor of 1.5 to minimise scaling is likely to be challenged more widely than just in France. Operators should be able to calculate the risk to efficiency that this will cause and plan accordingly.

If a chemical solution to carbonate scaling is to be pursued the river authority should be asked whether they would prefer the effluent to have the same pH as the water taken from the river. If so, the addition of sulphuric acid to the circulating waters will change some of the generated carbonate to sulphate (so reducing plant scaling). Many rivers naturally contain calcium sulphate from gypsum substrates, so objections should be few.

The published data on the solubility of calcium sulphate shows it is unlikely to precipitate at the CF's considered here, but as some sulphate was detected in power station calcium phosphate scales, rig studies should be performed to look for co-precipitation.

Addition of acids to a system should only be performed after its vulnerability to corrosion has been assessed.

The CaMass© Monitor (Patent pending)

A combined monitor and predicter of scaling is under development. Based on this Concept of Scaling it subtracts the mass of scalants leaving the system (measured at the purge or any convenient place in the circulating water system) from the mass entering the system. This is the mass precipitating. The mass depositing is calculated from the known engineering parameters from its construction specification (TEMA) and a model of its over specification, so that any design excess can be utilised. This excess can be interrogated via a plugin accessory to run "What If" scenarios.

IN MEMORIAM: INDEXES

I come not to bury Indexes but to praise them. They may still have use for corrosion prediction but their use for predicting scaling in recirculating evaporatively cooled industrial waters should be replaced by the Scaling Concept described here.

Scaling Indexes were the only tool available to chemists to warn their engineering colleagues that conditions controlled by nature were collaborating against them to precipitate scales where they could cause energy losses. Even a peremptory look at a heated water pipe would indicate that the hot end would have some scale in it even if the cold end had none. So, a link between temperature and scale was born. Scaling Indexes have comprised four or five parameters (Ca, alk, pH, conductivity or TDS and temperature) which were known to increase in summer and decrease in winter. The rate at which such scales grew was so small (mass divided by time) that no analytical technique could differentiate between inlet and outlet water concentrations. There was no way that an assay of carbonate could provide a quantitative mass balance as carbon dioxide was being continuously vented up the cooling towers from the conversion of soluble bicarbonates into insoluble carbonates.

Scaling Indexes seemed to correlate with scale, but the correlation could not be quantitatively corroborated. Is this where the myth of bulk supersaturation was created? That argument was used against the rig to study the amelioration of calcium phosphate scaling. Fortunately, it didn't matter whether or not the rig would grow scale at a representative rate; all the rig needed to do was to have the facility to grow scale at the same rate in two tubes, so that one tube could be dosed with a scale ameliorant to assess its effectiveness in parallel with undosed river Trent water.

As described here, whilst testing industrial scaling inhibitors against untreated river Trent water it was possible to perform an assay of what went where – a mass balance, as phosphate anions were not lost up the cooling towers. It was possible to differentiate between the net mass deposited in the heated tubes and the mass precipitated (lost from solution) in the system. This paved the way for a reassessment of the calcium carbonate models that had led to the creation of scaling indexes.

Until this work was carried out, Scaling Indexes were relied on by chemists and engineers as a qualitative indication of scaling. Now, it is possible to move from the qualitative to the reasonably quantitative (after all, the rate of scale deposition is not constant within a tube bundle and temperature is only measured as an average of water exiting the bundle). It is possible to monitor and record precipitation rate (in kilos/day or whatever is most useful). It is possible to quantitatively answer "What If" questions, such as, "What If the river authority demands a reduction of heat discharged to the river, what will happen to the rate of scaling". See CaMass© Monitor for details.

Scaling Indexes have been relied upon in the absence of anything better, but it is time to move on to a different concept of scaling.

Long rest the Scaling Index. Perhaps to be retired to swimming pools around the world.

CONCLUSIONS

The processes governing scaling by calcium salts depend upon the anions. Calcium phosphate scaling can be interpreted as a particulate process when water enters the warm, high pH, saturated environment of a cooling tower pond and forms a precipitate. That process is influenced by residence time of the water and salts in the ponds. Some of that precipitate adheres to the heated surfaces of the condenser tubes (linked to Reynolds Number), even after some is swept off due to shear stress.

Calcium carbonate on the other hand seems to leave solution at the heated surface, with minimal effect from residence time, as far as these few Concept of Principle experiments in the study of precipitation have determined. These limited experiments however have not eliminated the possibility that residence time can have an effect on deposition and also pH of the circulating water. Further work is needed.

Caution should be used when looking at older papers and skepticism employed if the conclusions are based on the reaction between calcium chloride and an alkali (sodium bi/carbonate) which has different kinetics from those of removing carbon dioxide from calcium bicarbonate, as happens in cooling towers. Further caution should be used if there is reference to a long induction period which may have been caused by thermal measurements of scaling and rig over design.

RESUMÉ

- Calcium carbonate and phosphate do not exhibit supersaturation.
- Scaling has no significant induction period.
- The Purge and Circulating Water analyses are the same.
- Scale is measured in mass per tube.
- Scaling *can be* studied in a 1/10th size rig.
- Scaling cannot be quantified from the development of Scaling Indexes
- Scaling can be quantified from the Concept of subtracting the effluent mass from the influent mass of calcium.
- Scaling is a Production Process.

Further Work

What has been shown in this paper is that scaling can be studied in a1/10th size rig. Rig work is needed to quantify calcium carbonate deposition under a variety of industrial turbulence and shear conditions. To that end, the end plates of a rig should accommodate various diameters of tubing. To measure deposition, it will be necessary to create representative precipitation conditions, incidentally producing a quantitative precipitation algorithm of use to industry. The aim is to predict scale deposition rate but in the absence of hydraulic data, the first step is to predict precipitation rate.

It is known that the solubility of a molecule is influenced by other material in solution. Total material in solution may be characterised by measuring TDS (total dissolved solids) or Conductivity. Thus, these need to be measured in future experiments to assess their effects.

It has still to be verified but this author postulates that silt does not deposit without scale to act as a binder under the turbulent regime of flow in condenser tubes. The mean size of both calcium phosphate scale and silt was 3.5 microns with 50% between 2 and 6 microns for amorphous scale, from Cottam power station.

The difference between the effects on scaling of half-life and the number of times an aliquot of water passes through the heated tube needs to be examined under more controlled conditions.

The scales from power stations along the Trent containing phosphate also contained sulphate despite the published solubility of calcium sulphate not being exceeded, thus some co-precipitation seems to occur. Experiments need to be performed to see whether calcium sulphate co-precipitates with calcium carbonate scales.

Whilst all the experiments described here relate to the move from qualitative precipitation (scaling indexes) to quantitative precipitation and deposition mass rates, the real problem is reduction in heat transfer. Impairment of heat transfer needs to be correlated with scaling rates for different scales.
The work could develop the concept of "temporal solubility" – defining what controls the concentration of the remaining soluble calcium species at any time in its residence within the system.

Subscripts

In   as entering the system
Out   as exiting the system
CW   as circulating within the system
     These last two are identical. See Figure 1

NOMENCLATURE

CF	ratio of Cl_{CW} / Cl_{In}	
D	Deposition rate (PO_4)	kg/s
M	Precipitation rate (PO_4)	
N	Number of times that an aliquot of water circulates before discharge	
P	Purge Rate	m^3/s
Q	make up rate	m^3/s
Re	Reynolds number	-
τ	Shear stress	
T	Temperature	°C
$t_{1/2}$	cooling water mean residence time	Hrs
V✓	System Volume	m^3
[X]	concentration of species X	kg/m^3

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